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Nonlinear optical properties in ZnSe crystals

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ABSTRACT

The two photon absorption (TPA) coefficient (β) and third order nonlinear optical susceptibility ($\chi^{<3>}$) of ZnSe crystals were investigated using the transmission and degenerate four wave mixing (DFWM) methods. The experimental results show that imaginary part of third order nonlinear optical susceptibility ($\chi^{<3>}$) decrease with increase of free carriers (n) and the absolute value of third order nonlinear optical susceptibility increase with increase of free electron concentration (n).

Keywords: degenerate four wave mixing, optical nonlinearities, third order nonlinear optical susceptibility, two photon absorption, crystals

1. INTRODUCTION

Wide band gap $A^{II}B^{VI}$ compounds are very attractive materials for optoelectronics devices, such as light emitting diodes, surface emitting lasers, waveguides and modulators[1], in the visible or ultraviolet region of the spectrum. In particular, ZnSe, as a semiconductor with a direct band gap of 2.67 eV at room temperature, is an important material for use in optoelectronics applications.

Knowledge of the optical properties of ZnSe crystals is especially important in the searching and analysis of laser structures and waveguiding devices in the whole visible field.

In this work, we present an experimental investigation of optical nonlinearity in ZnSe crystals using the nonlinear transmission and degenerate four wave mixing (DFWM) methods[2].

2. EXPERIMENTAL

The DFWM response of the crystals was measured with a mode-locked Q-switched Nd:YAG laser with 30 ps pulses width, 1 Hz repetition rate, and 532 nm wavelength. We assume that the intensity of the laser beam at the input face of the sample is the Gaussian distribution in space and time. Measurements were performed at room temperature. Intentionally undoped ZnSe crystals were grown from the melt by the modified high-pressure Bridgman method under an argon over pressure of 11 MPa using ZnSe powder as a starting material. The crystals were cut into 1 mm thick plates parallel to (111) crystallographic plane. The obtained samples have been annealed in liquid zinc at different temperatures between 830° and 920°. After this process, the samples were mechanically polished and chemically etched. The final thickness of the ZnSe crystals was about 0.73 mm. The measurements of resistivity, Hall mobility and carrier concentration were performed with the Van der Pauw method using indium dots as the contacts. The investigated monocrystal ZnSe belong to point group $\bar{4}3m$ for which spatial symmetry imposes restrictions on the form of the fourth-rank electric susceptibility tensor.

3. RESULTS AND DISCUSSION

In general third order nonlinear optical susceptibility ($\chi^{<3>}$) is considered to be a complex quantity: $\chi^{<3>} = \chi^{<3>}{}' + i\chi^{<3>}{}''$, where the real part of third order nonlinear optical susceptibility ($\chi^{<3>}{}'$) describe the nonlinear refractive index change

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which will be extracted from degenerate four wave mixing (DFWM) measurements, and the imaginary part of third order nonlinear optical susceptibility ($\chi^{<3>}{}''$) is related to the two photon absorption (TPA) coefficient (β) calculated from transmission measurement.

The knowledge of the two photon absorption (TPA) spectrum of semiconductors is important for development of all-optical switching elements, because TPA imposes a fundamental limitation on the performance of such devices[3]. The TPA takes place when the laser photon energy ($h\nu$) is larger than half the energy band gap and lower than the energy band gap of crystal ($E_g/2 < h\nu < E_g$). The relation between the laser photon energy and energy band gap of the investigated crystals allows us to determine the TPA coefficient (β) for ZnSe crystals[4].

We used the nonlinear transmission measurements to obtain the TPA coefficient (β) related to the imaginary parts of the third order nonlinear optical susceptibility ($\chi^{<3>}$).

The experimental result for ZnSe crystal is presented in Fig. 1. As can be seen, the solid line shows the best fit with theoretical formula (1) to the experimental data. We can notice that all samples studied reveal a strong nonlinear absorption decreasing with an increase of the free electron concentration.

$$T = \frac{I_T(L)}{I_1(0)} = \frac{\alpha \exp(-\alpha L)}{\alpha + \beta I_1 (1 - \exp(-\alpha L))} \tag{1}$$

where I_1 is the incident intensity, I_T is the transmitted intensity, α is the linear absorption coefficient, L is the thickness of the crystal and β is the TPA coefficient.

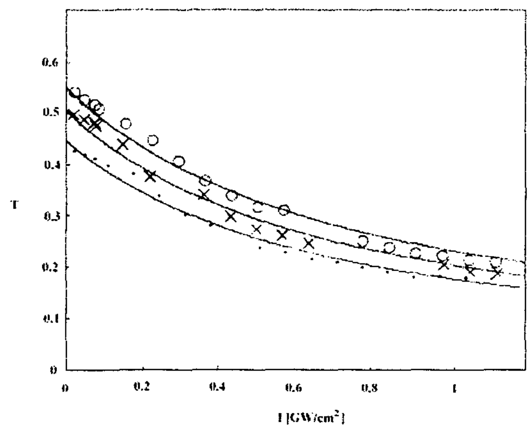

Fig. 1. The transmission as a function of the incident intensity I_1 at 532 nm. The (.), (x) and (o) represent the experimental data for n-type ZnSe crystals annealed in the temperatures 870°C, 890°C, 920°C, respectively.

We assumed Gaussian distribution of the laser intensity I_1 and took into account Fresnel reflection, which reduced the laser intensity in the crystal by the factor $(1-R)^2$, where $R = \left(\frac{1-n}{1+n}\right)^2$ is the reflection coefficient of the air-semiconductor interface[3]. The values of TPA coefficient (β) extracted from dependencies of Fig. 1 and theoretical formula (1) are presented in Table 1. We can see that for the crystal the straight line of Fig. 1 intercepts the ordinate axis and their value is lower than the unity. So it intercepts the ordinate axis at values of $\exp(-\alpha L)$ corresponding to the values of the linear absorption coefficient (α) listed in Table 1. We can also observe that the linear absorption (α) coefficient decreases as the free electron concentration increases. The linear absorption is due, among other reason, to the impurity levels in the band gap. The imaginary part of $\chi^{<3>}$ for ZnSe crystals was calculated by the equation (2) and is presented in Table 1:

$$\chi^{<3>}{}'' = \frac{n^2 c\lambda}{48\pi^3}\beta \qquad (2)$$

where n is the refractive index and $\chi^{<3>}{}''$ is the imaginary part of third order nonlinear optical susceptibility.

Table 1: The values of linear absorption (α) and nonlinear absorption (β) coefficients, the absolute value and imaginary parts of third order nonlinear optical susceptibility ($\chi^{<3>}$) for ZnSe for different free carriers concentration (n) and different temperatures (T)

Table. 1.

Crystals	T $[{}^{\circ}C]$	$n\cdot 10^{-15}$ $[cm^{-3}]$	α $[cm^{-1}]$	β $[cm/GW]$	$Im(\chi^{<3>})$ $[esu]$	$\lvert\chi^{<3>}\rvert$ $[esu]$
ZnSe-1	870	74	5	14.9	$1.1\cdot 10^{-11}$	$5.7\cdot 10^{-12}$
ZnSe-2	890	130	3.3	13.7	$1.07\cdot 10^{-11}$	$6.2\cdot 10^{-12}$
ZnSe-3	920	290	2.1	12.3	$0.96\cdot 10^{-11}$	$7.1\cdot 10^{-12}$
ZnSe	-	-	-	5.5 [7]	$0.64\cdot 10^{-11}$ [8]	$1.8\cdot 10^{-12}$ [8]

The absolute value of $\chi^{<3>}$ for ZnSe crystals was estimated using DFWM method. In the DFWM measurement (Fig.2), two counter-propagating strong pump beams (<1> and <2>) are incident on the sample with a third weaker probe beam (<3>), which incidents at the angle θ ($\theta = 12^{\circ}$) with respect to the pump beams. The pump beams interfere inside the sample to form the refractive index grating from which the third beam diffracts to form a conjugate signal (designated by <4>) that retraces the probe path[5]. The incident beams of the same frequency (ω) are temporally and spatially overlap in the sample and their intensities satisfy the relations: $I_1(z=0) = I_2(z=L)$ and $I_3 = 6\cdot 10^{-2} I_1$. All the DFWM measurements were taken using the parallel (xxxx) configuration. The phase conjugate signal was detected by a photo-multiplier tube (PM). A portion of the input beam was picked off and measured by a photodiode (V_c) to monitor the input energy. The photodiode and conjugate signals were averaged and displayed by a Tektronix TDS 3054 Digital Phosphor Oscilloscope.

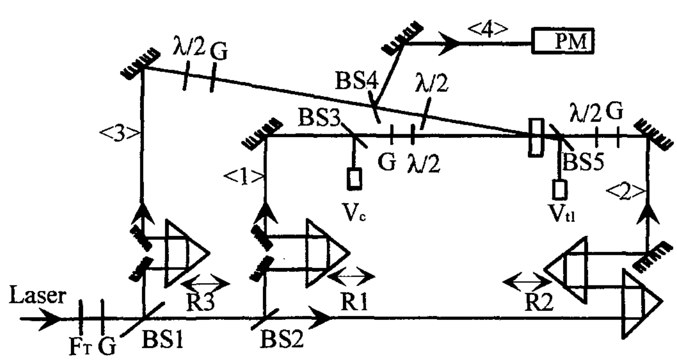

Fig. 2. The experimental set-up of DFWM method: <1> and <2> - pump beams; <3> - probe beam; <4> - fourth beam; S - sample; F_T - neutral filter; R_1, R_2, R_3 -delay lines; G - glan prism; V_c, V_t - control photodiodes; PM - photo-multiplier tube.

The experimental and theoretical results of DFWM reflectivity (R) are presented in Fig. 3. The DFWM reflectivity (R) was calculated from the propagation equation of the four interacting beams deduced from the Maxwell equations using slowly varying amplitude approximations and took into account linear and nonlinear absorption and the transformation from the crystallographic axis to laboratory axis. The DFWM reflectivity (R) can be expressed as follows[6]:

$$R = \frac{I_4(0)}{I_3(0)} = \frac{K^2}{\left[q\coth(qL) - \frac{\phi}{2}\right]^2} \quad (3)$$

where $q^2 = \left(\frac{\phi}{2}\right)^2 - K^2$, and $K^2 = \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \left(\chi'^2 + \chi''^2\right) I_1 I_2$, $\phi = -\alpha - 2\beta(I_1 + I_2)$.

χ' and χ'' are the real and imaginary parts of third order nonlinear optical susceptibility ($\chi^{<3>}$), respectively.

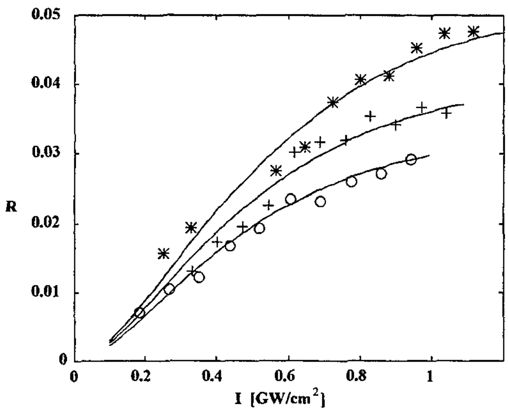

Fig. 3. DFWM reflectivity (R) as a function of the incident intensity I_1. The (*), (+) and (o) represent the experimental data for n-type ZnSe crystals annealed in the temperatures 920°C, 890°C, 870°C, respectively.

As can be seen in Fig. 3, the solid line shows the fit with theoretical formula (3) to the experimental data. The values of absolute value of $\chi^{<3>}$ estimated from the dependencies of Fig. 3 and theoretical formula (3) are presented in Table 1. We obtain that the absolute value of third order nonlinear optical susceptibility ($\chi^{<3>}$) tends to increase with electron concentration (n). However the relative changes of the real part of third order nonlinear optical susceptibility ($\chi^{<3>}$) with electron concentration remain smaller than those of the imaginary part of third order nonlinear optical susceptibility ($\chi^{<3>}$).

4. CONCLUSIONS

We evaluated the TPA coefficient (β) and calculated the imaginary part of $\chi^{<3>}$ from the nonlinear transmission at 532 nm. It is found that the nonlinear absorption and the imaginary part of $\chi^{<3>}$ decreases with increasing of free carriers (n). We also evaluated the absolute value of $\chi^{<3>}$ for studied crystals using DFWM method. The absolute value of $\chi^{<3>}$ increases with increase of free electron concentration. We observe that the linear absorption coefficient α decreases as free electron concentration increases. Heat treatment of crystals improves their structure due to the elimination of some impurity levels in the band gap, which causes a decrease in linear absorption in ZnSe. The experimental values of the TPA coefficient (β) for ZnSe crystals presented in this work are about two-three times higher than for polycrystals of ZnSe ($\beta = 5.5[cm/GW]$, $\beta = 5.8[cm/GW]$)[7]. Also the experimental values of $\chi^{<3>}$ in our work are about two times larger than for polycrystals of ZnSe ($Im(\chi^{<3>}) = 0.64 \cdot 10^{-11}[esu]$ and $Re(\chi^{<3>}) = 1.8 \cdot 10^{-11}[esu]$)[8].

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REFERENCES

1. E. Snoeks, T. Marshall, J. Petruzzello, M.D. Pashley, L.L. Chao, and G.S. Cargill, "Diffusion lengths of carriers in *n*- and *p*-type ZnMgSSe cladding layers of green laser diodes", *J. Appl. Phys.* 84, pp. 3611-3616, 1998

2. R.W. Boyd, *Nonlinear optics* Academic Press Inc., 1992

3. J.A. Bolger, A.K. Kar, B.S. Wherrett, R.DeSalvo, D.C.Hutchings, and D.J.Hagan, "Nondegenerate two-photon absorption spectra of ZnSe, ZnS and ZnO", *Optics Comm.* 97, pp. 203-209, 1993

4. K.R. Allakhverdiev, "Two-photon absorption in layered $TlGaSe_2$, $TlInS_2$, $TlGaS_2$ and GaSe crystals", *Solid State Comm.* 111, pp. 253-257, 1999

5. A.A. Said, M. Sheik-Bahae, D.J. Hagan, E.J. Canto-Said, Y.Y. Wu, J. Young, T.H. Wei, and E.W. Van Stryland, "Nonlinearities in semiconductors for optical limiting", SPIE, Vol. 1307 Electro-Optical Materials for Switches, Coatings, Sensor Optics, and Detectors, pp. 294-301, 1990

6. B. Sahraoui, G. Rivoire, and W. Bala, "Influence of doping and annealing temperature in n-type semiconductors ZnSe and ZnSe:Ag on two-photon absorption and third-order susceptibility", *J. Luminescence* 72/74, pp. 829-831, 1997

7. D.C. Hutchings, and E.W. Van Stryland, "Nondegenerate two-photon absorption in zinc-blende semiconductors", *J. Opt. Soc. Am. B* 9, pp. 2065-2074, 1992

8. Y. Guo, L. Yang, A.D. Walser, and R. Dorsinville, "Experimental observation of all-optical defection using forward degenerate four-wave mixing in ZnSe", *Optics Comm.* 119, pp. 139-142, 1995